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APPLICATION NUMBER: ***10/925,600***
FILING DATE: ***August 24, 2004***
RELATED PCT APPLICATION NUMBER: ***PCT/US05/01103***

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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	SEN3USA
First Inventor	Arup K. SenGupta et al.
Title	METHOD OF MANUFACTURE AND USE OF HYBRID ANION ....
Express Mail Label No.	ED 227893744 US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Commissioner for Patents, P.O. Box 1450, Alexandria VA 22313-1450

1. ☑ Fee Transmittal Form (e.g., PTO/SB/17) *(Submit an original and a duplicate for fee processing)*
2. ☐ Applicant claims small entity status. See 37 CFR 1.27.
3. ☑ Specification [*Total Pages* 24]
   (preferred arrangement set forth below)
   - Descriptive title of the invention
   - Cross Reference to Related Applications
   - Statement Regarding Fed sponsored R & D
   - Reference to sequence listing, a table, or a computer program listing appendix
   - Background of the Invention
   - Brief Summary of the Invention
   - Brief Description of the Drawings *(if filed)*
   - Detailed Description
   - Claim(s)
   - Abstract of the Disclosure
4. ☑ Drawing(s) *(35 U.S.C. 113)* [*Total Sheets* 19]
5. Oath or Declaration [*Total Sheets* 2]
   a. ☑ Newly executed (original or copy)
   b. ☐ Copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional with Box 18 completed)*
      i. ☐ DELETION OF INVENTOR(S)
      Signed statement attached deleting inventor(s) name in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
6. ☑ Application Data Sheet. See 37 CFR 1.76
7. ☐ CD-ROM or CD-R in duplicate, large table or Computer Program *(Appendix)*
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      ii. ☐ Paper
   c. ☐ Statements verifying identity of above copies

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ACCOMPANYING APPLICATION PARTS

9. ☐ Assignment Papers (cover sheet & document(s))
10. ☐ 37 CFR 3.73(b) Statement *(when there is an assignee)* ☑ Power of Attorney
11. ☐ English Translation Document *(if applicable)*
12. ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
13. ☐ Preliminary Amendment
14. ☑ Return Receipt Postcard (MPEP 503) *(Should be specifically itemized)*
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16. ☐ Nonpublication Request under 35 U.S.C. 122 (b)(2)(B)(i). Applicant must attach form PTO/SB/35 or its equivalent.
17. ☐ Other: ....

18. If a CONTINUING APPLICATION, *check appropriate box, and supply the requisite information below and in the first sentence of the specification following the title, or in an Application Data Sheet under 37 CFR 1.76:*

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: ....

Prior application information: Examiner ____________ Art Unit: ____________

For CONTINUATION OR DIVISIONAL APPS only; The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

19. CORRESPONDENCE ADDRESS

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FEE TRANSMITTAL for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 385.00

Complete if Known	
Application Number	
Filing Date	
First Named Inventor	Arup K. SenGupta et al.
Examiner Name	
Art Unit	
Attorney Docket No.	SEN3USA

METHOD OF PAYMENT *(check all that apply)*

☑ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☑ Deposit Account:

Deposit Account Number: 08-3040

Deposit Account Name: Howson and Howson

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1001	770	2001	385	Utility filing fee	385.00
1002	340	2002	170	Design filing fee	
1003	530	2003	265	Plant filing fee	
1004	770	2004	385	Reissue filing fee	
1005	160	2005	80	Provisional filing fee	

SUBTOTAL (1) ($) 385.00

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

			Extra Claims		Fee from below		Fee Paid
Total Claims	19	-20** =	0	X	0.00	=	0.00
Independent Claims	3	- 3** =	0	X	0.00	=	0.00
Multiple Dependent						=	

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
1202	18	2202	9	Claims in excess of 20
1201	86	2201	43	Independent claims in excess of 3
1203	290	2203	145	Multiple dependent claim, if not paid
1204	86	2204	43	** Reissue independent claims over original patent
1205	18	2205	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) 0.00

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FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
1051	130	2051	65	Surcharge - late filing fee or oath	
1052	50	2052	25	Surcharge - late provisional filing fee or cover sheet	
1053	130	1053	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for *ex parte* reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	420	2252	210	Extension for reply within second month	
1253	950	2253	475	Extension for reply within third month	
1254	1,480	2254	740	Extension for reply within fourth month	
1255	2,010	2255	1,005	Extension for reply within fifth month	
1401	330	2401	165	Notice of Appeal	
1402	330	2402	165	Filing a brief in support of an appeal	
1403	290	2403	145	Request for oral hearing	
1451	1,510	1451	1,510	Petition to institute a public use proceeding	
1452	110	2452	55	Petition to revive - unavoidable	
1453	1,330	2453	665	Petition to revive - unintentional	
1501	1,330	2501	665	Utility issue fee (or reissue)	
1502	480	2502	240	Design issue fee	
1503	640	2503	320	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee under 37 CFR 1.17(q)	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	770	2809	385	Filing a submission after final rejection (37 CFR 1.129(a))	
1810	770	2810	385	For each additional invention to be examined (37 CFR 1.129(b))	
1801	770	2801	385	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

Other fee (specify) ____________

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SUBMITTED BY

(Complete *(if applicable)*)

Name (Print/Type)	George A. Smith, Jr.	Registration No. (Attorney/Agent)	24,442	Telephone	215-540-9200
Signature	[signature]			Date	08/24/04

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METHOD OF MANUFACTURE AND USE OF HYBRID ANION EXCHANGER FOR SELECTIVE REMOVAL OF CONTAMINATING LIGANDS FROM FLUIDS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from provisional application 60/538,131, filed January 21, 2004.

FIELD OF THE INVENTION

[0002] The invention relates to the manufacture and application of hybrid anion exchangers for selective removal of contaminants from fluids.

BACKGROUND OF THE INVENTION

[0003] It is universally recognized that a fixed-bed sorption process is operationally simple, requires virtually no start-up time, and is forgiving toward fluctuations in feed compositions. However, in order for a fixed-bed process to be viable and economically competitive, the sorbent must exhibit high selectivity toward the target contaminant, must be durable, and must be amenable to efficient regeneration and reuse.

[0004] Ideally, the removal of the target contaminant should not cause major changes in pH or in the composition of the influent water. In this regard, both amorphous and crystalline Hydrated Fe Oxide (HFO) show strong sorption affinity toward both As(III) and As(V) oxyacids and oxyanions through ligand exchange in the coordination spheres of structural Fe atoms. Recent investigations using extended X-ray absorption fine structure spectroscopy (EXAFS) confirmed that As(III) and As(V) species are selectively bound to the oxide surface through formation of inner-sphere complexes. HFO particles also exhibit high sorption affinities toward phosphate, natural organic

matters, selenite and other anionic ligands. FIG. 1 shows an illustration of the binding of various solutes onto hydrated Fe(III) oxides or HFO. Commonly encountered competing ions, such as chloride or sulfate can be sorbed only through Coulombic interaction or formation of outer-sphere complexes. Thus, they exhibit poor sorption affinity toward HFO particles. In comparison, ligands such as arsenite, monovalent arsenate, divalent arsenate, phosphate, etc. are sorbed strongly through Lewis acid-base interaction or formation of inner-sphere complexes.

[0005] The traditional process of syntheses, although straightforward, produces only very fine submicron HFO particles which are unusable in fixed beds, permeable reactive barriers, or any flow-through systems, because of excessive pressure drops, poor mechanical strength and unacceptable durability. In order to overcome this problem, strong-acid cation exchangers have previously been modified to dope/disperse HFO particles for removal of arsenic. Iron-loaded cation exchange resins and alginates have also been tried for the removal of selenium and arsenic oxyanions. Although cation exchanger-loaded hydrated Fe(III) oxide (HFO) particles are capable of removing arsenates or phosphates, their removal capacities are reduced because the gel phase of the cation exchanger is negatively charged due to the presence of sulfonic acid groups. Consequently, arsenates or As(V) oxyanions and phosphates are rejected due to the Donnan co-ion exclusion effect, and dispersed HFO particles in the gel phase are not accessible to dissolved anionic ligands for selective sorption.

[0006] When macroporous cation exchangers were used as the host materials, arsenic removal capacity was not high, but on the order of 750 μg As/g of sorbent. However, when

a gel-type cation exchanger was used for dispersing HFO particles, the resulting material was ineffective altogether.

[0007] FIG. 2 shows a column run effluent history where a gel-type cation exchanger was loaded with eight percent HFO present as Fe. Arsenic breakthrough took place almost immediately. Thus, the material had practically no arsenic removal capacity. We have observed that HFO particles, when encapsulated within cation exchange sites as illustrated in FIG. 3, are not accessible to arsenates or other anionic ligands for selective sorption. However dispersion of HFO particles within a cation exchanger material is a relatively straightforward process.

[0008] Objects of the invention, therefore, are to provide a novel and more effective medium for the selective removal of arsenic species and other ligands from aqueous solutions, and to provide a method for effectively loading hydrated iron oxides onto an anion exchange resin.

BRIEF SUMMARY OF THE INVENTION

[0009] Unlike cation exchangers, anion exchangers have fixed positively charged functional groups. Thus, anionic ligands can easily permeate in and out of the gel phase without encountering the Donnan co-ion exclusion effect. If HFO particles are dispersed within a polymeric anion exchanger bead, arsenic or ligand removal capacity can be significantly increased. On the other hand, forming hydrated Fe(III) oxides within an anion exchange resin poses a major challenge due to positively charged quaternary ammonium functional groups. Consequently, heretofore, no way was known to achieve successful dispersion of HFO particles within a polymeric anion exchanger.

[0010] The synthesis of a selective adsorbent in accordance with the invention comprises the steps of reacting a material that exhibits anion exchange behavior with an anionic oxidant to produce an intermediate, and reacting, with the intermediate, a solution of a metal salt capable of being oxidized, thereby precipitating and dispersing a salt of the metal throughout the intermediate by the action of the oxidant, and producing an adsorbent.

[0011] The step of reacting the material that exhibits anion exchange behavior with an anionic oxidant is preferably carried out by passing a solution of the anionic oxidant through the material. The step of reacting a solution of a salt of a metal with the intermediate is carried out by passing a solution of the salt through the intermediate, thereby oxidizing the metal, and causing precipitation and dispersion of another salt, in which the metal is in a higher oxidation state than in the original salt. The step of reacting a solution of a metal salt with the intermediate may be followed by the step of washing the adsorbent with an organic solvent, preferably acetone, and then drying the adsorbent.

[0012] In preparing the adsorbent, improved results may be realized by repeating the steps of reacting a material that exhibits anion exchange behavior with an anionic oxidant, and reacting a solution of a salt of a metal with the intermediate.

[0013] The material that exhibits anion exchange behavior is preferably a polymeric anion exchange resin, and may comprise weak base organic ion exchange resin beads containing primary, secondary or tertiary amine groups or a mixture thereof. Alternative preferred materials are strong base organic ion exchange resin beads containing quaternary ammonium groups with a positively charged

nitrogen atom, and organic ion exchange resin beads having a polystyrene or polystyrene/divinylbenzene matrix.

[0014] The preferred metal salt is a solution of ferrous salt, and the preferred anionic oxidant is a permanganate, or a hypochlorite.

[0015] The adsorbent thus produced comprises a polymeric anion exchange resin containing dispersed particles of an oxygen-containing compound of iron, and is capable of selective removal of ligands from a fluid stream brought into contact with the adsorbent. The adsorbent is especially effective in removing ligands such as arsenates, arsenites, chromates, molybdates, selenites, and vanadates from a stream of drinking water, groundwater, industrial process water or industrial effluent.

[0016] In a preferred embodiment, an adsorbent bed for the selective removal of ligands from the aqueous solution is prepared by passing a solution containing an oxidizing anion such as a permanganate, persulfate or hypochlorite, through a bed of polymeric anion exchange resin. Thereafter a solution of a ferrous salt, such as ferrous sulfate, is passed through the bed, thereby simultaneously desorbing the oxidizing anion and oxidizing the ferrous ion to a ferric ion. This causes precipitation, and uniform dispersion, of a solid, hydrated ferric oxide, within the polymeric anion exchange resin. Anionic ligands such as arsenates, chromates, oxalates, phosphates, phthalates, etc., can permeate in and out of the gel phase and are not subjected to the Donnan exclusion effect. Consequently, anion exchanger-supported HFO micro particles exhibit significantly greater capacity, in comparison with cation exchanger-supported particles, for removal of arsenates, arsenites, and other arsenic oxyanions, as well as other ligands.

[0017] Another advantage of the invention is that the physical properties of the anion exchange material can supply structural integrity to materials that are otherwise friable and weak. Thus, by dispersion of HFO particles into anion exchange materials, it is possible to synthesize a bed that exhibits superior materials properties when compared to HFO particles that, by themselves are subject to granulation and agglomeration. The improved physical robustness afforded by the use of an anion exchange material allows for use of HFO particles under more demanding conditions such as higher pressures, increased flow, etc. The improved physical robustness of the hybrid material also allows for effective regeneration and reuse of the bed, and reduces the need for backwashing and other maintenance measures common in the treatment of streams with hydrous metal oxides that are not supported by substrates.

[0018] Other objects, details and advantages of the invention will be apparent from the following detailed description when read in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 is a schematic diagram illustrating the binding of various solutes onto hydrated Fe(III) oxides;

[0020] FIG. 2 is a graph of the effluent history for arsenic during a column run using a hybrid cation exchanger gel;

[0021] FIG. 3 is a schematic diagram illustrating why an HFO doped cation exchange resin is unable to offer significant arsenic sorption capacity;

[0022] FIG. 4(a) and 4(b) are schematic diagrams illustrating first and second steps in the preparation of a hybrid anion exchanger sorbent;

[0023] FIGs. 5(a), 5(b) and 5(c) are respectively a photograph of macroporous, hybrid anion exchange sorbent particles, a scanning electron microphotograph of a sliced parent polymer bead, and a scanning electron microphotograph of a sliced hybrid anion exchange bead;

[0024] FIG. 6 is a schematic diagram of a set-up for fixed bed column runs and regeneration tests;

[0025] FIG. 7(a) is a graph showing the effluent histories for sulfate and arsenic during a column run with a parent anion exchanger in chloride form, showing early arsenic break-through;

[0026] FIG. 7(b) is a graph of the effluent history for arsenic during a column run using a macroporous hybrid cation exchanger;

[0027] FIG. 7(c) is a graph of the effluent history for arsenic during a column run using a macroporous hybrid anion exchanger;

[0028] FIG. 8 is a graph comparing the effluent histories for arsenic in a hybrid gel-type cation exchanger and a hybrid gel-type anion exchanger;

[0029] FIG. 9 is a graph comparing As(V) and silica breakthrough profiles during the treatment for groundwater using a freshly prepared, macroporous, hybrid anion exchanger;

[0030] FIG. 10 is a graph illustrating the arsenic concentration profile during typical regeneration of a hybrid anion exchange resin;

[0031] FIG. 11 is a graph of the effluent histories of As(V(an Cr(VI) during a column run using a macroporous hybrid anion exchanger;

[0032] FIG. 12 is a graph showing the concentration profiles of arsenic and chromium during regeneration of a macroporous hybrid anion exchanger;

[0033] FIG. 13 is a graph showing breakthrough profiles for phosphorous and other anions during a column run using a macroporous hybrid anion exchanger;

[0034] FIG. 14 is a graph showing the effluent histories for arsenic during two consecutive column runs using a macroporous hybrid anion exchanger with the same contaminated groundwater feed;

[0035] FIG. 15 is a graph showing the concentration of iron in the effluent during a column run using macroporous hybrid anion exchanger particles

[0036] FIGs. 16(a) and 16(b) are x-ray diffractograms of freshly prepared, and used, hybrid anion exchange particles, respectively;

[0037] FIG. 17 is a graph showing a comparison of vanadate effluent histories for a hybrid anion exchanger and a parent anion exchanger; and

[0038] FIG. 18 is a graph showing a comparison of molybdate effluent histories for a hybrid anion exchanger and a parent anion exchanger.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0039] Since Fe^{3+} and Fe^{2+} are cations, they are repelled by an anion exchanger's positively charged functional groups and cannot be loaded onto anion exchange resins. Thus, the technique, used previously for dispersing HFO particles within cation exchanger beads, is not applicable when anion exchanger beads serve as the host materials. We have discovered, however, that HFO particles can be

supported in anion exchanger by a series of steps, a preferred example of which is as follows.

[0040] As a first step, Permanganate anion (MnO_4^-) is loaded onto an anion exchange resin (for example A-500P, an anion exchange resin with quaternary ammonium functional groups in chloride form, available from The Purolite Company of Bala Cynwyd, Pennsylvania). The loading of the resin with permanganate anion is carried out by passing potassium permanganate solution (500 mg/L $KMnO_4$) through the bed. This may be carried out, for example by passing a 500 mg/L $KMnO_4$ solution through the bed to achieve the following reaction:

$$\overline{R(CH_3)_3N^+Cl^-} + MnO_4^- \leftrightarrow \overline{R(CH_3)_3\ N^+\ MnO_4^-} + Cl^-$$

$\overline{R(CH_3)_3N^+Cl^-}$ is an anion exchange resin with a quaternary ammonium functional group in chloride form.

[0041] Anion exchange resins from other manufacturers may of course be used. Particles sizes of the anion exchange resins are preferably in the range from 300 μm to 1000 μm.

[0042] The second step is concurrent permanganate desorption, Fe(II) oxidation and HFO formation within the anion exchanger. During this step, the permanganate loaded anion exchanger is brought into contact with 5% ferrous sulfate solution. Desorption of MnO_4^- by sulfate, reduction of MnO_4^- to $MnO_2(s)$ and oxidation of Fe^{2+} to Fe^{3+} and finally, precipitation of $Fe(OH)_3(s)$ within the anion exchanger beads, took place in accordance with the following:

MnO_4^- desorption:

$$\overline{2R(CH_3)_3N^+MnO_4^-} + SO_4^{2-} \leftrightarrow \overline{[R(CH_3)_3\ N^+]_2SO_4^{2-}} + 2MnO_4^-$$

Fe(II) oxidation and formation of Ferric Hydroxide:

$$MnO_4^- + 4H^+ + 3e^- \xrightarrow{\text{reduction}} \overline{MnO_2}(s) + 2H_2O$$

$$3Fe^{2+} \xrightarrow{\text{oxidation}} 3Fe^{3+} + 3e^-$$

$$3Fe^{3+} + 9OH^- \xrightarrow{\text{precipitation}} \overline{3Fe(OH)_3}\ (s)$$

overall: $MnO_4^- + 3Fe^{2+} + 2H_2O + 5OH^- \rightarrow MnO_2(s) + 3Fe(OH)_3(s)$

(The overbars and (s) denote solid phase.)

[0043] The third step is an acetone wash and drying. Anion exchanger beads from the second step are washed with acetone and dried in a furnace at 35°C for twelve hours.

[0044] The major steps of the process, that is, the first and second steps, are depicted in FIGs. 4A and 4B. These steps can be repeated to achieve greater Fe(III) loading. Also, the manganese content within the anion exchanger decreases with multiple cycles, and this is a desirable phenomenon from an application viewpoint. During the third step, the use of acetone reduced the dielectric constant of the water and enhanced the agglomeration of HFO submicron particles through suppression of surface charges. HFO agglomerates were irreversibly encapsulated within the spherical anion exchanger beads. Turbulence and mechanical stirring do not result in any noticeable loss of HFO particles.

[0045] Both gel and macroporous anion exchanger beads (Purolite A-400 and A-500P) were used in our study. Mass loading of HFO onto the anion exchanger varied from 10-15% as Fe; the manganese content was le ss than 1% by mass as

Mn. FIG. 5A shows Hybrid Anion Exchanger (HAIX) particles. FIG. 5B is a scanning electron microphotograph (SEM) of a sliced parent polymer bead, in which the presence of macropores can be readily observed. FIG. 5C shows a sliced HAIX particle containing HFO nanoparticles.

[0046] While the polymeric anion exchanger beads exhibit excellent hydraulic properties and durability during fixed-bed column runs, the dispersed HFO microparticles serve as active sorbents for target ligands.

[0047] By way of example, details of the steps carried out in a typical laboratory synthesis of hybrid anion exchanger particles are as follows.

[0048] In a 4.0 liter container filled with 500 mg/L solution of potassium permanganate, 30 g of Purolite anion exchanger resin were immersed the solution for 30 minutes with intermittent stirring. The resin loaded with permanganate was rinsed twice with deionized water. Thereafter, the permanganate-loaded resin was immersed in 1.0 liter of 5.0% (w/v) ferrous sulfate solution and shaken for four hours. The modified resin (hybrid anion exchanger) was then rinsed several times with deionized water. These steps were repeated for a second and third cycle of iron loading. Following each cycle, a sample of about 50 mg of the hybrid anion exchanger was taken for iron and manganese content analysis.

[0049] The hybrid resin was rinsed with deionized water and acetone, and then dried in an oven at 35° C for 12 hours. Both macroporous and gel-type anion exchangers from The Purolite Company, namely, Purolite A-500P and A-400, were used as the parent materials. The iron and manganese loading of HAIX particles were found by digesting twice with 10% sulfuric acid for 24 hours at room temperature.

The iron and manganese values at the end of each cycle of preparation were as follows:

For HAIX-M (Macroporous parent resin)

Cycle	Iron content* (mg/g of hybrid anion exchanger)	Manganese content* (mg/g of hybrid anion exchanger)
1	57.3	31.3
2	130.1	5.0
3	162.0	1.2

For HAIX-G (Gel parent resin)

Cycle	Iron content* (mg/g of hybrid anion exchanger)	Manganese content* (mg/g of hybrid anion exchanger)
1	35.0	4.5
2	52.2	0.8
3	60.0	0.2

* Based on dried hybrid anion exchanger beads

[0050] Approximately ten different batches of HAIX-M and five different batches of HAIX-G have been synthesized. The iron content for HAIX-M after three cycles varied between 120-175 mg Fe/g, while the iron content for HAIX-G was between 70-100 mg Fe/g.

[0051] It was observed that the white color of the macroporous anion exchange resin changed to purple during loading with permanganate (MnO_4^-) ion. Following the addition of ferrous sulfate solution, the purple color of the resin gradually changed to light brown. A uniform light brown color characterizes the completion of hydrated ferric oxide or HFO formation within the resin beads. Approximately four hours are needed for this step to be completed.

[0052] Laboratory tests were conducted to prepare HAIX using sodium hypochlorite (NaOCl) solution following the same experimental protocol. By way of example, details of the steps carried out in laboratory synthesis of hybrid anion exchanger particles using hypochlorite ions (OCl^-) are as follow.

[0053] In a 4.0 liter container filled with 500 mg/L of NaOCl solution, 30 g of macroporous anion exchanger resin were immersed into the NaOCl solution for 30 min with intermittent stirring. The resin loaded with hypochlorite anion was then rinsed twice with deionized water. The hypochlorite-loaded resin was then immersed in 1.0 L of 5.0% (w/v) ferrous sulfate solution and shaken for four hours. The modified resin (hybrid anion exchanger) was then rinsed several times with deionized water.

[0054] The above steps were repeated for a second and third cycle of iron loading. Following each cycle, a sample of about 50 mg of the hybrid anion exchanger was taken for iron content analysis.

[0055] The hybrid resin was rinsed with deionized water and acetone, and then dried in an oven at 35°C for 12 hours. The iron loading was found to be as follows:

Cycle	Iron Content* (mg/g of hybrid anion exchanger)
1	10.0
2	25.0
3	40.0

* Based on dried hybrid anion exchanger beads.

[0056] Since the iron loading was significantly less with hypochlorite than with permanganate, the performance evaluation of HAIX during fixed-bed column runs and other sorption studies were carried out on products obtained using permanganate as oxidizing agent.

[0057] In the evaluation of the performance of HAIX the following experimental protocol was used.

[0058] A series of fixed-bed experiments were carried out to evaluate the As(III) and As(V) removal capacities of HAIX. The experimental set-up is illustrated in FIG. 6, where contaminated water from a reservoir 20 was pumped by a pump 22 into a column 24 containing HAIX beads 26 over a glass fiber layer 28. Regenerant in reservoir 30 was pumped into the column by pump 32. The effluent was collected in effluent sample tubes 34.

[0059] Using this test set-up, tests were also conducted to validate the ability of HAIX to remove chromate, phosphate and natural organic matter. The following results are noteworthy:

[0060] FIGs. 7A - 7C provide As(III) effluent histories for three separate column runs under nearly identical conditions using respectively Parent Anion Exchanger Purolite A-500P in chloride form in FIG. 7A, HFO loaded macroporous cation exchanger in FIG. 7B, and Hybrid Anion

Exchanger or HAIX in FIG. 7C. The abscissa (C/Co) represents the fraction of the influent concentration present at the exit of the column.

[0061] As shown in FIG. 7A, the parent anion exchanger was unable to remove As(III). The empty bed contact time (EBCT) was 4.5 minutes. The influent solution contained 100 μg/L As(III), 170 mg/L SO_4^{2-}, 90 mg/L Cl^-, 100 mg/L HCO_3^-, and had a pH of 6.2. Arsenic broke through immediately, and long before the sulfate breakthrough.

[0062] As shown in FIG. 7B, the HFO loaded cation exchanger removed As(III) over more than 2000 bed volumes, with a breakthrough concentration of 10 μg/L at about 2500 bed volumes. In this case, the EBCT was 3.1 minutes. The influent solution contained 100 μg/L As(III), 122 mg/L SO_4^{2-}, 70 mg/L Cl^-, 100 mg/L HCO_3^-, and had a pH of 7.2.

[0063] In the experiment depicted in FIG. 7C, the experimental parameters were the same as in FIG. 7A. That is, the EBCT was 4.5 minutes, and the e influent solution contained 100 μg/L As(III), 170 mg/L SO_4^{2-}, 90 mg/L Cl^-, 100 mg/L HCO_3^-, and had a pH of 6.2., As illustrated in FIG. 7C, the HAIX, or HFO loaded anion exchanger, treated nearly 12,000 bed volumes of contaminated feed water before the arsenic concentration in the effluent reached 10 μg/L. The HAIX-M (Macroporouse hybrid anion exhanger offered a six-fold greater As(III) removal capacity over the HCIX-M (Macroporous hybrid cation exchanger).

[0064] To validate the hypothesis that the Donnan Co-ion exclusion effect in the host material significantly influences the arsenic removal capacity of hydrated iron oxide particles, one gel-type cation exchanger (HCIX-G, using Purolite C-100) and one gel-type anion exchanger (HAIX-G, using Purolite A-400) were loaded with iron oxide particles. Subsequently two column runs were carried out

separately for arsenic removal, using these two materials. The Fe content of the HAIX-G was 60 mg/g of HAIX-G, and the Fe content of the HCIX-G was 70 mg/g of HCIX-G. The tests were carried out under identical experimental conditions. The superficial liquid velocity (SLV) was 0.60 m/h, and the EBCT was 3.9 minutes. The influent contained 100 μg/L As(V), 120 mg/L SO_4^{2-}, 100 mg/L Cl^-, 100 mg/L HCO_3^-, and had a pH of 7.3

[0065] FIG. 8 shows the arsenic effluent histories for the two column runs. The hybrid cation exchanger offered practically no arsenic removal, even with a slightly higher iron content; the hybrid anion exchanger, or HAIX, on the contrary removed arsenic at well over 10,000 bed volumes, all other conditions being identical.

[0066] The groundwater in Albuquerque, New Mexico is contaminated with arsenic, and also contains a high level of dissolved silica. About twenty gallons of contaminated groundwater were collected from Albuquerque, and a column run was carried out using macroporous HAIX. The SLV was 0.83 m/h and the EBCT was 3.8 minutes. The influent contained 4.6 μg/L As(V), 33 mg/L of silica and 0.46 mg/L of phosphorus. The pH of the influent was 7.6.

[0067] FIG. 9 shows the effluent history for arsenic removal. Even with 33 mg/L of dissolved silica present in the contaminated water, arsenic removal was very good. Arsenic breakthrough of 10 parts per billion was observed after 7,200 bed volumes, while silica broke through from the column within 500 bed volumes.

[0068] An Arsenic loaded HAIX-M column can be very efficiently regenerated using a solution of 3% NaCl and 2% NaOH at a pH of 12.4 and with an EBCT of 5.6 minutes. As shown in FIG. 10, over 90% of the arsenic was desorbed within 10 bed volumes.

[0069] Arsenate and Chromate can be removed simultaneously, as illustrated in FIG. 11, which illustrates the effluent histories of AS(V) and Cr(VI) during a column run with a macroporous hybrid anion exchanger (HAIX-M). Here the EBCT was 3.8 minutes. The influent was a representative feedwater containing 100 μg/L As(V), 100 μg/L Cr(VI), 120 mg/L SO_4^{2-}, 125 mg/L Cl^-, and 100 mg/L HCO_3^-, and had a pH of 7.1. The HAIX column was fed with the representative synthetic feed water. The HAIX column was shown to be very effective in removing both Arsenic(V) and Chromium(VI) simultaneously up to nearly 2000 bed volumes.

[0070] Upon exhaustion, the column was regenerated using 2% NaOH and 3% NaCl. FIG. 12 shows the concentration profiles of arsenic and chromium during regeneration of the HAIX-M at an EBCT of 3.9. The desorption of arsenate and chromate was shown to be very efficient.

[0071] FIG. 13 illustrates the removal of phosphate using the hybrid anion exchanger. A HAIX column was fed with a feed solution containing phosphate along with other commonly encountered anions. Specifically the influent contained 4.43 mg/L phosphate (as P), 90 mg/L Cl^-, 42 mg/L SO_4^{2-}, 56 mg/L NO_3^-, and 78 mg/L HCO_3^1, and had a pH of 7.1. the EBCT was 3.3 minutes. The effluent history for P, as depicted in FIG. 13, confirms the ability of HAIX to remove phosphate selectively in the presence of other competing anions, namely, chloride and sulfate.

[0072] One HAIX column was run for three successive cycles. After each cycle, the column was regenerated with 2% NaOH and 3% NaCl. FIG. 14 shows the effluent histories for arsenic in two successive column runs using groundwater collected from a contaminated site in Ontario, Canada. The SLV was 1.58 m/h and the EBCT was 1.56 minutes. The

influent contained 430 µg/L As, 280 µg/L P, 3.0 mg/L TOC, 11.9 mg/L SO_4^{2-}, 6.4 mg/L Cl^-, 21.9 mg/L NO_3^-, and had a pH of 7.2. The arsenic effluent histories remained essentially the same. These results provide evidence that HAIX can be regenerated and reused for multiple cycles without a significant loss in arsenic removal capacity.

[0073] FIG. 15 shows the concentration of total iron released during a lengthy column run under conditions in which the SLV was 0.70 m/h and the EBCT was 4.5 minutes. The influent contained 100 µg/L As(III), 170 mg/L SO_4^{2-}, 90 mg/L Cl^-, 100 mg/L HCO_3^-, and had a pH of 6.2. The iron concentration at the exit of the column was quite low (less than 3 µg/L) for nearly 15,000 bed volumes. The loss of iron from HAIX is negligible (30 µg/g HAIX-M) compared to its total capacity (120-150 mg Fe/g HAIX).

[0074] It is plausible that, with aging and continued usage, amorphous HFO particles could gradually become more crystalline leading to the formation of goethite, hematite, etc. However, FIGs. 16A and 16B show a comparison of X-ray diffraction (XRD) patterns of freshly prepared (FIG. 16A) versus used (FIG. 16B) HAIX samples. Both patterns are quite similar, with very minor changes. It is unlikely that HFO nanoparticles embedded in the anion exchanger underwent any structural changes.

[0075] FIG. 17 illustrates the performance of a hybrid anion exchanger in accordance with the invention in removing Vanadate from tap water spiked with 3 mg/L Vanadate as V. Two effluent histories are shown, one for the parent anion exchanger, and the other for the hybrid anion exchange material. As shown by the graph, the vanadate almost immediately began to pass through the parent anion exchanger, whereas, in the case of the hybrid anion exchange material, measurable amounts of vanadate

began to be detected only after about 3000 bed volumes, and remained at a level below 200 parts per billion at 8000 bed volumes.

[0076] Performance of the hybrid anion exchanger in accordance with the invention in the removal of molybdates was also effective as shown by FIG. 18. Two column runs were carried out, one using the parent anion exchanger and the other using the hybrid anion exchanger, on an influent consisting of tap water spiked with 3 mg/L of Molybdate as Mo. With the parent anion exchanger, Molybdate began to break through at about 100 bed volumes, and rose from a level of about 100 μg/L at about 300 bed volumes to about 1700 μg/L at 1300 bed volumes. On the other hand, in the case of the hybrid anion exchanger, Molybdate remained at a level below 100 μg/L up to about 1000 bed volumes and rose only to about 400 μg/L at 1300 bed volumes.

[0077] Numerous modifications can be made to the invention as described. As indicated previously, any of a wide variety of anion exchange resins can be used to carry out the selective removal of ligands. For example, as alternatives to strong base anion exchange resins having quaternary ammonium functional groups with a positively charged nitrogen atom, other anion exchange materials can be used, such as weak base organic ion exchange resin beads containing primary, secondary or tertiary amine groups or a mixture thereof; organic ion exchange resin beads having a polystyrene or polystyrene/divinylbenzene matrix; organic ion exchange resin beads having a polyacrylic matrix; organic or inorganic membranes; and polymeric fiber or fibrous anion exchange materials.

[0078] In principle, any anionic oxidizing agent can be used in place of permanganate. For example, in addition to hypochlorite, mentioned previously, other anionic oxidants,

for example persulfates, bromates and iodates, may be used. The intermediate, produced by reacting the anion exchange material with an anionic oxidant, may be reacted with a solution of an oxidizable salt of a metal, preferably a ferrous salt such as ferrous sulfate, ferrous ammonium sulfate, ferrous chloride or ferrous acetate. The hydrated iron oxide particles precipitated in the anion exchange material can take various forms, such as hematite, geothite, magnetite and ferrihydrite.

[0079] Still other modifications may be made to the apparatus and method described above without departing from the scope of the invention as defined in the following claims.

CLAIMS

1. A method for synthesizing a selective adsorbent comprises the steps of:

reacting a material that exhibits anion exchange behavior with an anionic oxidant to produce an intermediate; and

reacting, with said intermediate, a solution of a salt of a metal, said salt being capable of being oxidized, thereby precipitating and dispersing a salt of said metal throughout the intermediate by the action of the oxidant and producing an adsorbent.

2. A method according to claim 1, in which the step of reacting said material that exhibits anion exchange behavior with an anionic oxidant is carried out by passing a solution of said anionic oxidant through said material, and in which the step of reacting a solution of a salt of a metal with said intermediate is carried out by passing a solution of said salt through said intermediate.

3. A method according to claim 1, in which the step of reacting a solution of a salt of a metal with said intermediate is followed by the step of washing the adsorbent with an organic solvent.

4. A method according to claim 1, in which the step of reacting a solution of a salt of a metal with said intermediate is followed by the step of washing the adsorbent with acetone.

5. A method according to claim 1, in which the step of reacting a solution of a salt of a metal with said

intermediate is followed by the steps of washing and drying the adsorbent.

6. A method according to claim 1 in which, in preparing said selective adsorbent, said steps of reacting a material that exhibits anion exchange behavior with an anionic oxidant, and reacting a solution of a salt of a metal with said intermediate, are repeated.

7. The method according to claim 1, in which said material that exhibits anion exchange behavior is a polymeric anion exchange resin.

8. The method according to claim 1, in which said material that exhibits anion exchange behavior comprises weak base organic ion exchange resin beads containing primary, secondary or tertiary amine groups or a mixture thereof.

9. The method according to claim 1, in which said material that exhibits anion exchange behavior comprises strong base organic ion exchange resin beads containing quaternary ammonium groups with a positively charged nitrogen atom.

10. The method according to claim 1, in which said material that exhibits anion exchange behavior comprises organic ion exchange resin beads having a polystyrene or polystyrene/divinylbenzene matrix.

11. The method according to claim 1, in which the precipitated and dispersed salt of said metal is an oxygen-containing compound of iron.

12. The method according to claim 1, in which the solution of a salt of a metal is a solution of ferrous salt.

13. The method according to claim 1, in which said anionic oxidant is a permanganate.

14. The method according to claim 1, in which said anionic oxidant is a hypochlorite.

15. An adsorbent for the selective removal of ligands from fluids, said absorbent comprising a polymeric anion exchange resin containing dispersed particles of an oxygen-containing compound of iron.

16. A method of removing contaminants from a fluid stream, wherein said fluid stream is brought into contact with an adsorbent comprising an HFO-impregnated anion exchange material.

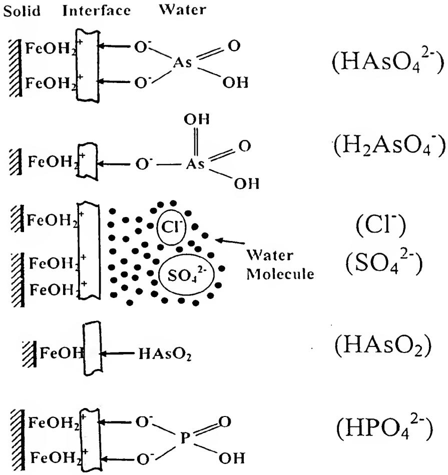
17. The method according to claim 16, in which said contaminants are ligands.

18. The method according to claim 16, in which said contaminants are ligands containing one or more anions from the group consisting of arsenates, arsenites, chromates, molybdates, selenites, and vanadates.

19. The method according to claim 16, in which said fluid stream is a stream of drinking water, groundwater, industrial process water or industrial effluent.

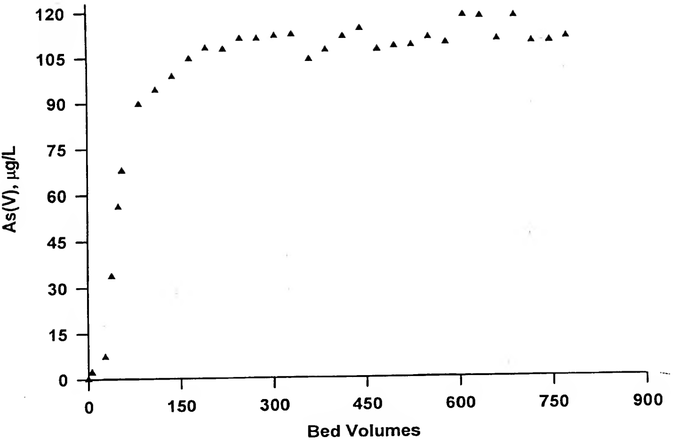
ABSTRACT OF THE DISCLOSURE

Polymeric anion exchangers are used as host materials in which hydrated Fe(III) Oxides (HFO) are irreversibly dispersed within the exchanger beads. Since the anion exchangers have positively charged quaternary ammonium functional groups, anionic ligands such as arsenates, chromates, oxalates, phosphates, phthalates can permeate in and out of the gel phase and are not subjected to the Donnan exclusion effect. Consequently, anion exchanger-supported HFO micro particles exhibit significantly greater capacity to remove arsenic and other ligands in comparison with cation exchanger supports. Loading of HFO particles is carried out by preliminary loading of the anion exchange resin with an oxidizing anion such as MnO_4^- or OCl^-, followed by passage of a Ferrous Sulfate solution through the resin.



Solid
Interface
Water
FeOH2+
FeOH2+
O-
O-
As
O
OH
(HAsO4 2-)
OH
O
FeOH2+
O-
As
OH
(H2AsO4-)
FeOH2+
Cl-
FeOH2+
FeOH2+
SO4 2-
Water Molecule
(Cl-)
(SO4 2-)
FeOH
HAsO2
(HAsO2)
FeOH2+
FeOH2+
O-
O-
P
O
OH
(HPO4 2-)

FIG. 1



120
105
90
75
60
45
30
15
0
As(V), µg/L
0
150
300
450
600
750
900
Bed Volumes

FIG. 2

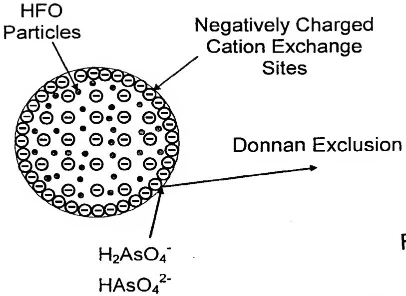


FIG. 3

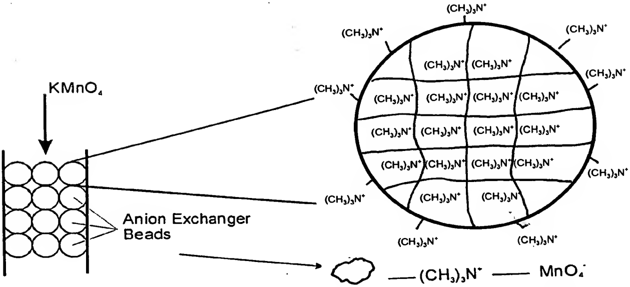
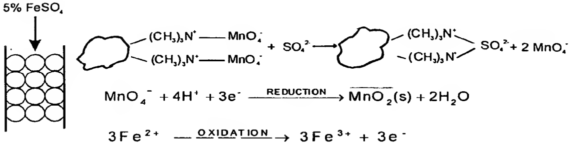


FIG. 4A



$$MnO_4^- + 4H^+ + 3e^- \xrightarrow{\text{REDUCTION}} \overline{MnO_2}(s) + 2H_2O$$

$$3Fe^{2+} \xrightarrow{\text{OXIDATION}} 3Fe^{3+} + 3e^-$$

$$3Fe^{3+} + 9OH^- \xrightarrow{\text{PRECIPITATION}} 3\overline{Fe(OH)_3}(s)$$

FIG. 4B

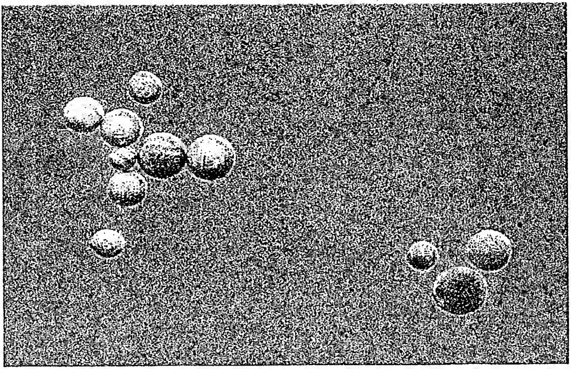


FIG. 5A

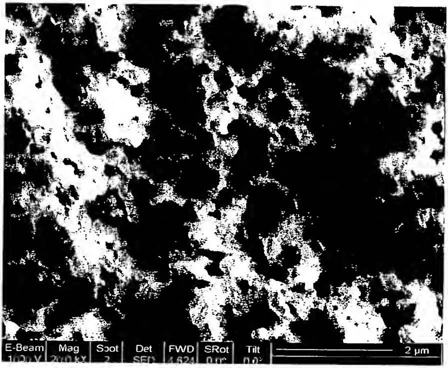


FIG. 5B

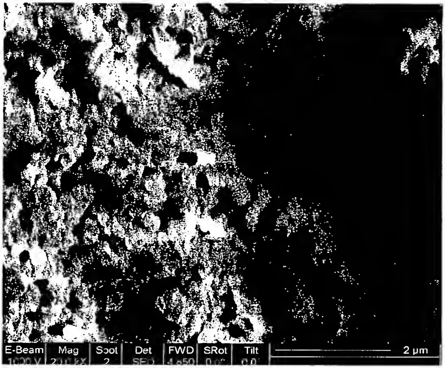


FIG. 5C

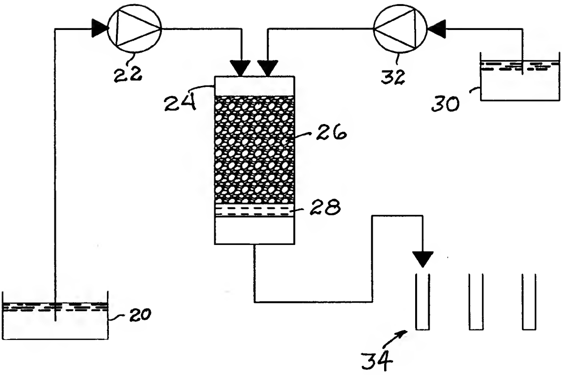
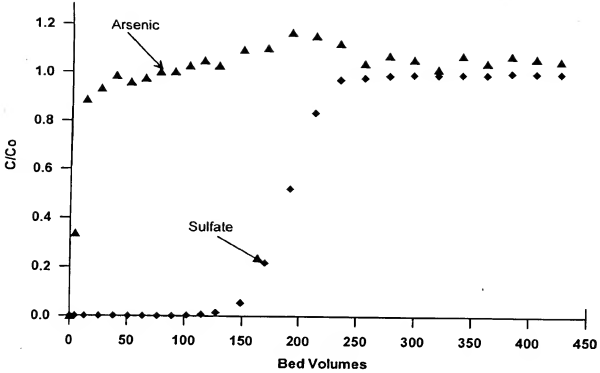
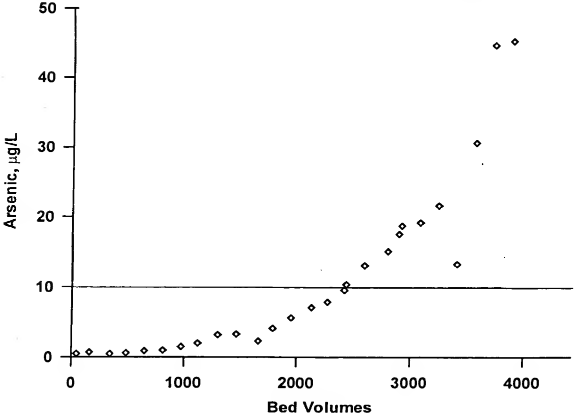


FIG. 6



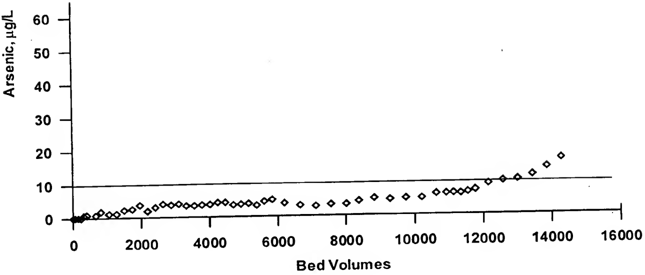
Arsenic
Sulfate
C/Co
Bed Volumes
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
350
400
450

FIG. 7A



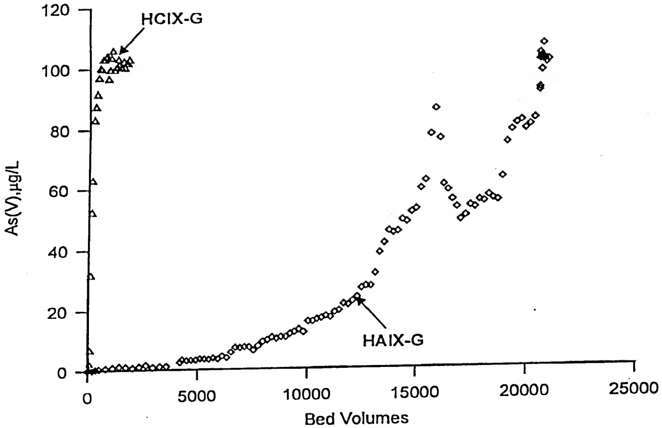
Arsenic, μg/L
Bed Volumes
50
40
30
20
10
0
0
1000
2000
3000
4000

FIG. 7B



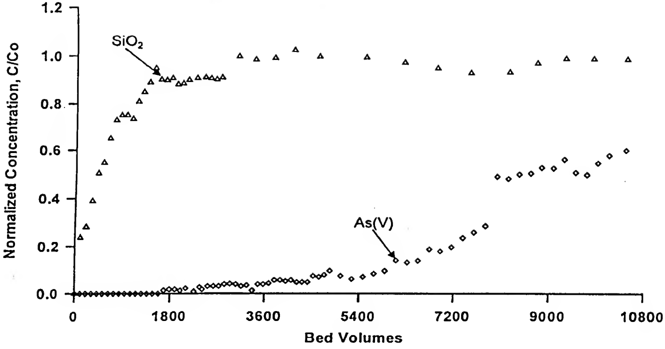
Arsenic, µg/L
60
50
40
30
20
10
0
0
2000
4000
6000
8000
10000
12000
14000
16000
Bed Volumes

FIG. 7C



120
100
80
60
40
20
0
HCIX-G
HAIX-G
As(V),μg/L
0
5000
10000
15000
20000
25000
Bed Volumes

FIG. 8



1.2
1.0
0.8
0.6
0.4
0.2
0.0
Normalized Concentration, C/Co
SiO_2
As(V)
0
1800
3600
5400
7200
9000
10800
Bed Volumes

FIG. 9

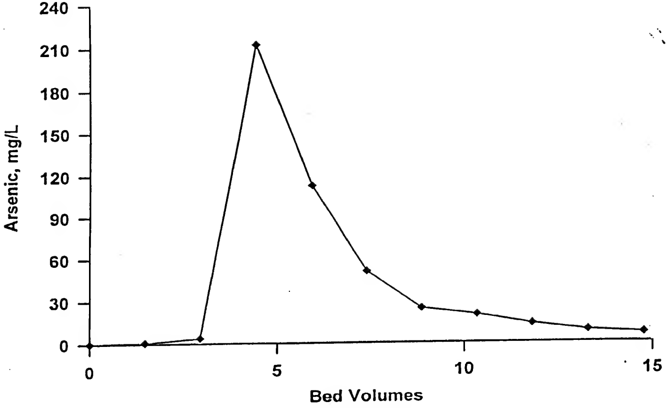


FIG. 10

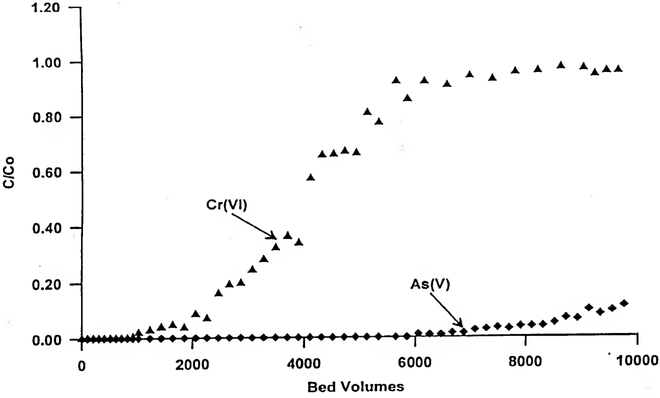

1.20
1.00
0.80
0.60
0.40
0.20
0.00
C/Co
Cr(VI)
As(V)
0
2000
4000
6000
8000
10000
Bed Volumes

FIG. 11

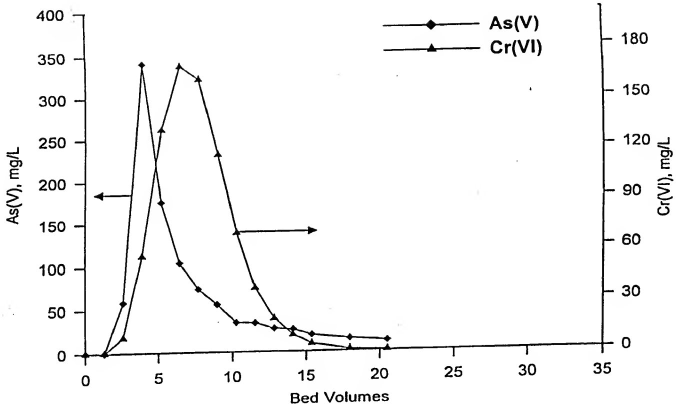
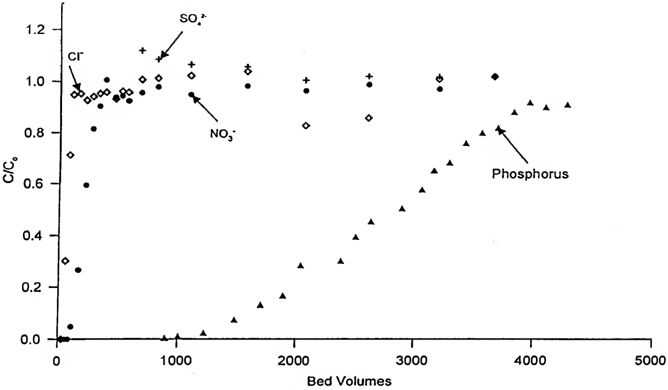

As(V)
Cr(VI)
400
350
300
250
200
150
100
50
0
As(V), mg/L
180
150
120
90
60
30
0
Cr(VI), mg/L
0
5
10
15
20
25
30
35
Bed Volumes

FIG. 12



1.2
1.0
0.8
0.6
0.4
0.2
0.0
C/Co
0
1000
2000
3000
4000
5000
Bed Volumes
SO4 2-
Cl-
NO3-
Phosphorus

FIG. 13

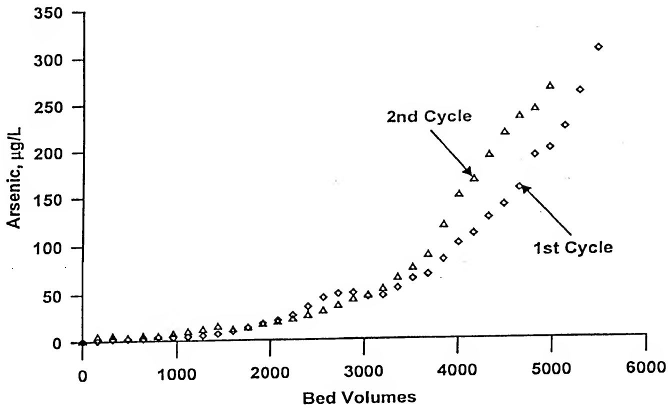

350
300
250
200
150
100
50
0
Arsenic, µg/L
0
1000
2000
3000
4000
5000
6000
Bed Volumes
2nd Cycle
1st Cycle

FIG. 14

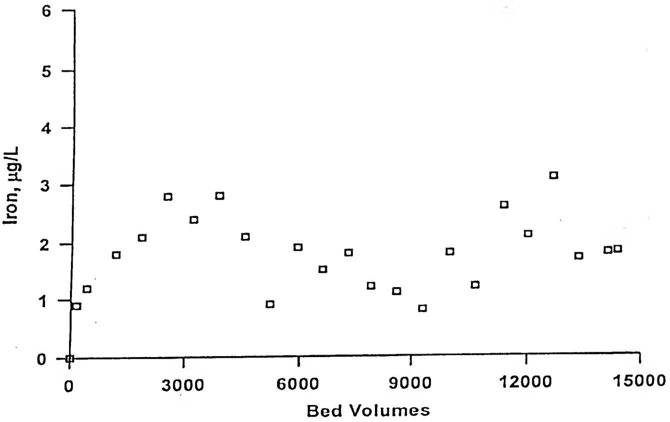


FIG. 15

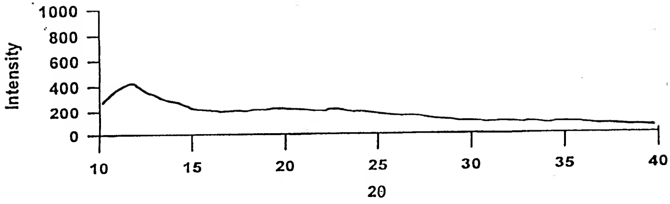


FIG. 16A

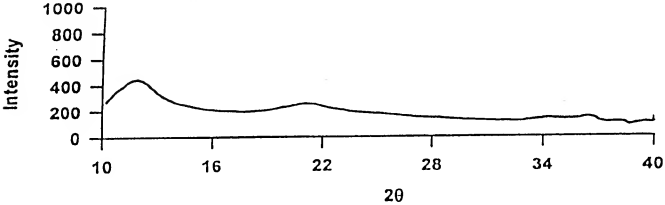
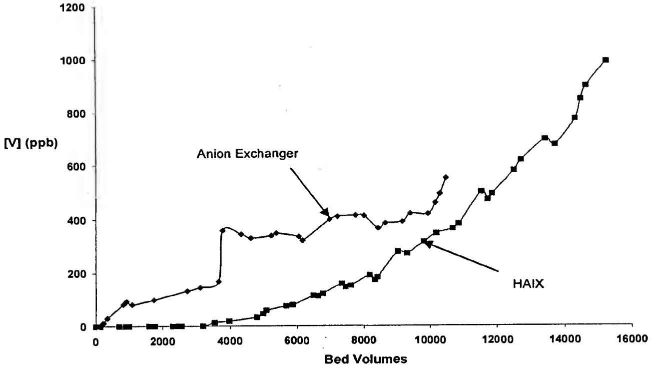
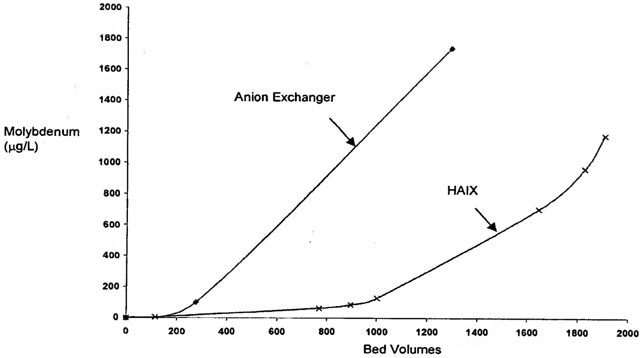


FIG. 16B



1200
1000
800
600
400
200
0
[V] (ppb)
Anion Exchanger
HAIX
0
2000
4000
6000
8000
10000
12000
14000
16000
Bed Volumes

FIG. 17



2000
1800
1600
1400
1200
1000
800
600
400
200
0
Molybdenum
(μg/L)
Anion Exchanger
HAIX
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Bed Volumes

FIG. 18

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

[X] Declaration Submitted With Initial Filing **OR** [ ] Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	SEN3USA
First Named Inventor	Arup K. SenGupta et al.
COMPLETE IF KNOWN	
Application Number	
Filing Date	
Art Unit	
Examiner Name	

I hereby declare that:

Each inventor's residence, mailing address, and citizenship are as stated below next to their name.

I believe the inventor(s) named below to be the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD OF MANUFACTURE AND USE OF HYBRID ANION EXCHANGER FOR SELECTIVE REMOVAL OF CONTAMINATING LIGANDS FROM FLUIDS

(Title of the Invention)

the specification of which

[X] is attached hereto

OR

[ ] was filed on (MM/DD/YYYY) [ ] as United States Application Number or PCT International Application Number [ ] and was amended on (MM/DD/YYYY) [ ] (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? Yes	No
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]

[ ] Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

PTO/SB/01 (08-03)
Approved for use through 07/31/2006. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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DECLARATION — Utility or Design Patent Application

Direct all correspondence to: [X] Customer Number: 00270	OR [ ] Correspondence address below		
Name			
Address			
City	State	ZIP	
Country	Telephone	Fax	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

NAME OF SOLE OR FIRST INVENTOR:	[ ] A petition has been filed for this unsigned inventor		
Given Name (first and middle [if any]) Arup K.	Family Name or Surname SenGupta		
Inventor's Signature Arup Sengupta			Date Aug 21, 2004
Residence: City Bethlehem	State Pennsylvania	Country U.S.	Citizenship U.S
Mailing Address 3286 Marchant Drive			
City Bethlehem	State Pennsylvania	ZIP 18017	Country U.S.

NAME OF SECOND INVENTOR:	[ ] A petition has been filed for this unsigned inventor		
Given Name (first and middle [if any]) Luis H.	Family Name or Surname Cumbal		
Inventor's Signature			Date 8/17/04
Residence: City Quito	State	Country Ecuador	Citizenship Ecuador
Mailing Address Avenida Cardenal de la Torre S12-74 Ciudadela Primero de Mayo (El Calzado)			
City Quito	State	ZIP	Country Ecuador

[ ] Additional inventors or a legal representative are being named on the ______ supplemental sheet(s) PTO/SB/02A or 02LR attached hereto.

PTO/SB/81 (06-04)
Approved for use through 11/30/2005. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

POWER OF ATTORNEY and CORRESPONDENCE ADDRESS INDICATION FORM

Application Number	
Filing Date	
First Named Inventor	Arup K. SenGupta et al.
Title	METHOD OF MANUFACTURING AND USE.
Art Unit	
Examiner Name	
Attorney Docket Number	SEN3USA

I hereby appoint:

[X] Practitioners associated with the Customer Number: 00270

OR

[ ] Practitioner(s) named below:

Name	Registration Number

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please recognize or change the correspondence address for the above-identified application to:

[X] The address associated with the above-mentioned Customer Number:

OR

[ ] The address associated with Customer Number:

OR

[ ] Firm or Individual Name					
Address					
Address					
City		State		Zip	
Country					
Telephone		Fax			

I am the:

[X] Applicant/Inventor.

[ ] Assignee of record of the entire interest. See 37 CFR 3.71.
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96)

SIGNATURE of Applicant or Assignee of Record

Signature	[signature]	Date	8/17/04
Name	Luis H. Cumbal	Telephone	
Title and Company			

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below*.

[X] *Total of 2 forms are submitted.

PTO/SB/81 (06-04)
Approved for use through 11/30/2005. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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POWER OF ATTORNEY and CORRESPONDENCE ADDRESS INDICATION FORM

Application Number	
Filing Date	
First Named Inventor	Arup K. SenGupta et al.
Title	METHOD OF MANUFACTURE AND USE..
Art Unit	
Examiner Name	
Attorney Docket Number	SEN3USA

I hereby appoint:

[X] Practitioners associated with the Customer Number: 00270

OR

[ ] Practitioner(s) named below:

Name	Registration Number

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please recognize or change the correspondence address for the above-identified application to:

[X] The address associated with the above-mentioned Customer Number:

OR

[ ] The address associated with Customer Number:

OR

[ ] Firm or Individual Name					
Address					
Address					
City		State		Zip	
Country					
Telephone		Fax			

I am the:

[X] Applicant/Inventor.

[ ] Assignee of record of the entire interest. See 37 CFR 3.71.
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96)

SIGNATURE of Applicant or Assignee of Record

Signature	Arup Sengupta	Date	Aug 21, 2009
Name	Arup K. SenGupta	Telephone	
Title and Company			

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more then one signature is required, see below*.

[X] *Total of 2 forms are submitted.

APPLICATION DATA SHEET

Application Information

Application Type::	Regular
Subject Matter::	Utility
Suggested Classification::	
Suggested Group Art Unit::	
CD-ROM or CD-R?::	None
Number of CD disks::	
Number of Copies of CDs::	
Sequence Submission?::	
Computer Readable Form (CRF)?::	
Number of Copies of CRF::	
Title::	METHOD OF MANUFACTURE AND USE OF HYBRID ANION EXCHANGER FOR SELECTIVE REMOVAL OF CONTAMINATING LIGANDS FROM FLUIDS
Attorney Docket Number::	SEN3USA
Request for Early Publication::	No
Request for non-Publication::	No
Suggested Drawing Figure::	
Total Drawing Sheets::	19
Small Entity::	Yes
Latin name::	
Variety denomination name::	
Petition Included?::	No
Petition Type::	
Licensed US Govt. Agency::	
Contract or Grant Numbers::	
Secrecy Order in Parent Application::	No

Applicant Information

Applicant Authority Type::	Inventor
Primary Citizenship Country::	US
Status::	Full Capacity
Given Name::	Arup
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Country of Mailing Address::	US
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Postal or Zip Code of Mailing Address::	

Correspondence Information

Correspondence Customer Number::	00270
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Country of Mailing Address::	US
Postal or Zip Code of Mailing Address::	19477
Telephone::	215-540-9200
Telefacsimile::	215-540-5818
E-Mail Address::	gasmith@howsonandhowson.com

Representative Information

Representative Customer Number::	00270	

Domestic Priority Information

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	An application claiming the benefit under 35USC119(e)	60/538,131	01/21/2004

Foreign Priority Information

Country::	Application Number::	Filing Date::	Priority Claimed::

Assignee Information

Assignee Name::	Arup K. SenGupta
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State or Province of Mailing Address::	PA
Country of Mailing Address::	US
Postal or Zip Code of Mailing Address::	18017